

# PATENT SPECIFICATION

1,093,943



DRAWINGS ATTACHED

1,093,943

Inventor: ROBERT ELLIS KNOWLTON

Date of filing Complete Specification: Sept. 28, 1964.

Application Date: Oct. 7, 1963.

No. 39401/63.

Complete Specification Published: Dec. 6, 1967.

© Crown Copyright 1967.

Index at acceptance:—C5 E (D2E, D2F, D2G, D3)

Int. Cl.:— C 10 g 9/48

## COMPLETE SPECIFICATION

### Reforming Hydrocarbons

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company of Imperial Chemical House, Millbank, London, S.W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the reforming of hydrocarbons particularly for the purpose of making synthesis gases of low methane content. In the conventional production of synthesis gases by reforming hydrocarbons the hydrocarbons mixed with steam or carbon dioxide or both are subjected to a primary reforming process over a catalyst at a high temperature, and there results a gas (to be referred to hereinafter as primary reformer gas) consisting essentially of hydrogen, carbon monoxide, carbon dioxide and methane. The methane is objectionable since it merely acts as an inert diluent, increasing gas pumping costs without taking part in synthesis reactions. It has therefore become common practice to decrease the methane concentration in a secondary reforming stage, that is, by adding oxygen to the gas, allowing partial combustion to take place, and bringing the gas mixture to chemical equilibrium at the resulting higher temperature, for example by passing it over a suitable catalyst; the methane content which results is then characteristic of the methane-steam or methane-carbon dioxide reaction equilibrium at the temperature of the secondary reforming stage. Such a practice however is not entirely satisfactory if the methane content of the primary reformer gas is high, owing to the amount of combustion of gas which is necessary to supply the heat for the methane-steam or methane-carbon dioxide reactions, which are endothermic processes. If air is used as the source of oxygen the gas becomes diluted with nitrogen, which is useful (if its concentration is correct) for a gas to be used in ammonia production, but is objectionable if the gas is

to be used for the production of hydrogen or for the synthesis of only organic compounds for example methanol. The methane content of primary reformer gas is higher the higher the pressure at which the process is conducted, hence the problem of keeping its concentration down becomes more difficult to solve with the modern trend towards higher pressures for example of 30 atmospheres and above. The methane content is lower the higher the temperature at which the process is conducted: however the limitations of materials of construction prevent sufficiently high temperatures from being used in conventional primary reforming processes. The methane content is also lower the higher the proportion of steam or carbon dioxide used at the primary reforming stage: however for economic reasons it is desirable to keep the steam or carbon dioxide ratio as low as possible.

We have now discovered a new process and apparatus by which synthesis gases of low methane content can be produced without a serious incidence of the above-mentioned unsatisfactory features.

According to the invention there is provided a process of producing synthesis gases which comprises reacting a hydrocarbon feedstock with steam or carbon dioxide or both in a first reaction zone to give a primary reformer gas containing methane and passing the primary reformer gas into a second reaction zone at a higher temperature than that at which the primary reformer gas was produced, the said second reaction zone being heated by indirect heat exchange with a heat transfer fluid at a pressure differing by not more than 10 atmospheres from the pressure of the primary reformer gas stream.

The invention thus includes a process in which the heat transfer fluid, which most conveniently consists of fuel-combustion product, is kept separate from the synthesis gas stream. However preferably the fuel-combustion products are at least partly and preferably

50

55

60

65

70

75

80

85

90

wholly mixed with the synthesis gas stream and eventually brought to chemical equilibrium with it at the said higher temperature. In particular the gas stream issuing from the second reaction zone is itself the fuel. It is of course only partly combusted to produce the required high temperature: such a partial combustion stage is substantially the same as the secondary reforming stage already referred to. Alternatively a part of the raw primary reformer gas stream (that is, gas before it has passed through the second reaction zone) can be by-passed and combusted, whereafter its hot combustion products are mixed with the gas stream issuing from the second reaction zone and brought to chemical equilibrium. As a further alternative, which may be employed alone or in combination with combustion of primary reformer gas hydrocarbon feedstock, which may be the same as or different from the hydrocarbon feedstock used to make the primary reformer gas, may be combusted, whereafter the resulting hot combustion products are mixed with the gas stream issuing from the second reaction zone and brought to chemical equilibrium.

In another form of the process of the invention the second reaction zone of one synthesis gas plant is heated by partial combustion of the gas issuing from the primary reforming stage or the second reaction zone of another synthesis gas plant.

In all these preferred forms of the invention the transfer of heat to the second reaction zone should preferably take place during or shortly after the attainment of chemical equilibrium in the gas containing the combustion products: if it takes place before the attainment of chemical equilibrium the temperature at which equilibrium is attained is decreased and consequently the methane content of the gas is increased. The invention can however be operated with heat transfer before the attainment of equilibrium provided the temperatures are suitably increased.

The second reaction zone or the zone in which the combustion products and the gas from the second reaction zone are brought to equilibrium thus preferably contains a catalyst, for example a supported transition metal reforming catalyst.

The temperature of the primary reforming stage is conveniently in the range 400 — 950°C. especially 600 — 800°C. Temperatures chosen from this range can be used with pressures as high as 100 atmospheres employing available constructional materials. The temperature can if desired be low enough for the primary reforming steps to be autothermic or exothermic.

The temperature of the second reaction zone may be considerably higher than that of the primary reforming stage since it is heated by gas at substantially the same pressure, so that there is very little strain on this containing

vessel due to pressure difference. The temperature may be for example 800 — 1000°C. when the primary reformer gas stream is at 20 — 60 for example 30 atmospheres pressure gauge, using readily available plant construction materials.

The process of the invention is especially useful for primary reformer gas stream pressures of above 20 atmospheres and especially 20 — 60 atmospheres gauge.

Owing to the high temperatures attainable in the second reaction zone, the steam ratio (that is, the number of molecules of steam per carbon atom present in the feed hydrocarbon) can be comparatively low, for example 1.5 — 3, without giving rise to excessive methane formation. In order to take the best advantage of the low equilibrium percentage of methane, the catalyst used in the primary reforming stage preferably should be of a kind having a low tendency to cause the formation of carbon, for example catalysts as described in our United Kingdom Patent No. 953,877.

The process of the invention is applicable to a considerable variety of hydrocarbon feedstocks, in particular natural gas, liquefied petroleum gas and normally liquid hydrocarbons boiling at up to 350°C. especially 30°C. to 220°C., for example light petroleum distillates.

The invention provides also an apparatus for carrying out the preferred forms of the process of the invention, comprising an externally heated first reaction zone capable of containing one or more beds for a primary reforming catalyst, a second reaction zone downstream of the first and optionally capable of containing one or more beds for catalyst and one or more combustion chambers downstream of the second reaction zone, the said second reaction zone being adapted to be heated by indirect heat exchange with gases produced in the said chamber or chambers.

Preferably a third reaction zone, preferably capable of containing one or more beds for a secondary reforming catalyst, is situated downstream of the combustion chamber: it should however preferably not be downstream of the heat exchange surfaces of the second reaction zone.

The combustion chamber includes means for admitting oxygen or a gas containing free oxygen, whereby partial combustion of the primary reformer gas takes place. In another form the combustion chamber includes also means for admitting a fuel, for example the same hydrocarbon feedstock as is supplied to the primary reformer, as well as means for admitting oxygen or a gas containing free oxygen, means being present also to ensure that the hot combustion products of this fuel become mixed with the product of the second reaction zone.

Preferably the second reaction zone is formed by a set of tubes in a pressure vessel, the space outside the tubes being in commun-

70

75

80

85

95

100

105

110

115

120

125

130

- cation with the outlet from the third reaction zone. The third reaction zone is preferably in a refractory-lined pressure vessel, so as to heat the gas as much as possible and to prevent overheating of its metal outer walls. The apparatus is preferably so constructed that the hot gases after the combustion stage flow counter-current to the gases in the second reaction space.
- One form of the apparatus according to the invention is shown in diagrammatic section in the accompanying drawings. The apparatus consists of a refractory-lined shell 10 capable of withstanding a pressure of 30 atmospheres gauge, and fitted at the top with an inlet 12 for connecting to a source of primary reformer gas containing methane and excess steam or carbon dioxide or both. The inlet 12 leads by way of flexible connections 13 (known as "pigtails") to the header 14 from which are suspended tubes 16 which when the apparatus is in use are packed with a primary reforming catalyst. These constitute the second reaction space or zone. They are joined at the bottom by way of pigtails 17 to header 18, leading to the combustion chamber 20, which is equipped with an air inlet 22 and a fuel inlet 24. (The fuel inlet 24 is an optional feature, being required only when it is desired to combust raw primary reformer gas or reform further feedstock at this stage of the process). The combustion chamber 20 is constructed so as to effect thorough mixing of the fuel combustion products with the product of the second reaction zone or to ensure uniform partial combustion if additional fuel is not added at this stage. The outlet from the combustion chamber is in communication with the space 26 surrounding the tubes 16. The combustion chamber contains beds for catalyst 28 when the apparatus is in use, and these constitute the third reaction zone; this zone is upstream of the heat transfer surface of the second reaction zone (tubes 16). At the upper end of the space 26 is the outlet 30, which is connectable via waste-heat boilers and purification plant (for example carbon monoxide shift and carbon dioxide removal plant) to plant using the outlet gases.

*Example*

A desulphurised straight-run petroleum distillate having a boiling range 30°C. to 220°C. was vapourised, superheated to 430°C., mixed with superheated steam (2.64 molecules per atom of carbon in the hydrocarbon) at 310°C. and subjected to a primary reforming process at a weight hourly space velocity of 0.7 (liquid calculated with respect to hydrocarbon) and a pressure of 30 atmospheres absolute over a supported nickel catalyst in tubes by combustion gases at approximately atmospheric pressure.

The gas issuing from this part of the process was at 825°C. and contained excess steam,

carbon monoxide 12.6%, carbon dioxide 12.3%, hydrogen 59.0%, and methane 13.3%. This gas was then passed through a bed of similar supported nickel catalyst in a second set of tubes ("second reaction zone") heated externally by product gas at 29 atmospheres pressure absolute passing counter-current to the gas within the tubes. The gas leaving these tubes was at 950°C. and now contained only 1.8% of methane. The gas was then mixed with oxygen in the form of air preheated to 500°C. and passed into a combustion chamber and then over a supported nickel catalyst (the third reaction zone). Partial combustion took place and at the resulting high temperature further endothermic reaction of methane with steam took place. The product gas leaving the third reaction zone with the outside of the tubes of the second reaction zone where it gave up heat to the tubes and was itself cooled to about 960°C. The methane content of the product gas was 0.15% and its content of carbon monoxide, hydrogen and nitrogen were correct for a gas mixture to be treated to produce an ammonia synthesis gas.

**WHAT WE CLAIM IS:—**

1. A process of producing synthesis gases which comprises reacting a hydrocarbon feedstock with steam or carbon dioxide or both in a first reaction zone to give a primary reformer gas containing methane and passing the primary reformer gas into a second reaction zone at a higher temperature than that at which the primary reformer gas was produced, the said second reaction zone being heated by indirect heat exchange with heat transfer fluid at a pressure differing by not more than 10 atmospheres from the pressure of the primary reformer gas stream.
2. A process according to claim 1 in which the heat transfer fluid consists of fuel combustion products.
3. A process according to claim 2 in which the fuel combustion products are mixed with the synthesis gas stream.
4. A process according to any one of the preceding claims in which a gas stream issuing from the second reaction zone is the fuel and is partly combusted to produce the high temperature.
5. A process according to claim 4 in which further feedstock is added to the gas stream issuing from the second reaction zone.
6. A process according to claim 4 or claim 5 wherein the transfer of heat to the second reaction zone takes place during or shortly after the attainment of chemical equilibrium in the gas containing the combustion products.
7. A process according to any one of the preceding claims in which the temperature of the primary reforming stage is in the range 600 — 800°C.
8. A process according to any one of the preceding claims in which the temperature of

- the second reaction zone is in the range 800 — 1000°C.
- 5      9. A process according to any one of the preceding claims in which the primary reformer gas stream is at a pressure in the range 20 — 60 atmospheres.
- 10     10. A process according to any one of the preceding claims wherein the steam ratio is in the range 1.5 — 3.
- 15     11. A process according to any one of the preceding claims wherein the hydrocarbon feedstock is a light petroleum distillate boiling in the range 30 — 220°C.
12. A process substantially as described and as set forth in the foregoing Example.
13. An apparatus for carrying out a process according to any one or the preceding claims, which comprises an externally heated first reaction zone capable of containing one or more beds for a primary reforming catalyst, a second reaction zone downstream of the first and optionally capable of containing one or more beds for catalyst and one or more combustion chambers downstream of the second reaction zone, the said second reaction zone being adapted to be heated by indirect heat exchange with gases produced in the said chamber or chambers.
14. An apparatus according to claim 13 including a third reaction zone downstream of the combustion chamber.
15. An apparatus according to claim 14, in which the third reaction zone is not downstream of the heat exchange surfaces of the second reaction zone.
16. An apparatus according to claim 14 or claim 15, in which the third reaction zone is capable of containing one or more beds for a secondary reforming catalyst.
17. An apparatus according to any one of claims 13 to 16 in which the combustion chamber includes means for admitting a fuel, means for admitting oxygen or an oxygen-containing gas, and means for ensuring that the hot combustion products of the fuel become mixed with the product from the second reaction zone.
18. An apparatus according to any one of claims 13 to 17 in which the second reaction zone is formed by a set of tubes in a pressure vessel, the space outside the tubes being in communication with the outlet from the third reaction zone.
19. An apparatus according to any one of claims 14 to 18 in which the third reaction zone is in a refractory lined pressure vessel.
20. An apparatus according to any one of claims 13 to 19 so constructed that the hot gases after the combustion stage flow countercurrent to the gases in the second reaction zone.
21. An apparatus substantially as described and is shown in the drawing.
22. Synthesis gas whenever produced by a process according to any one of claims 1 to 12 or in an apparatus according to any one of claims 13 to 21.

Agent for the Applicants.  
WALTER SCOTT.

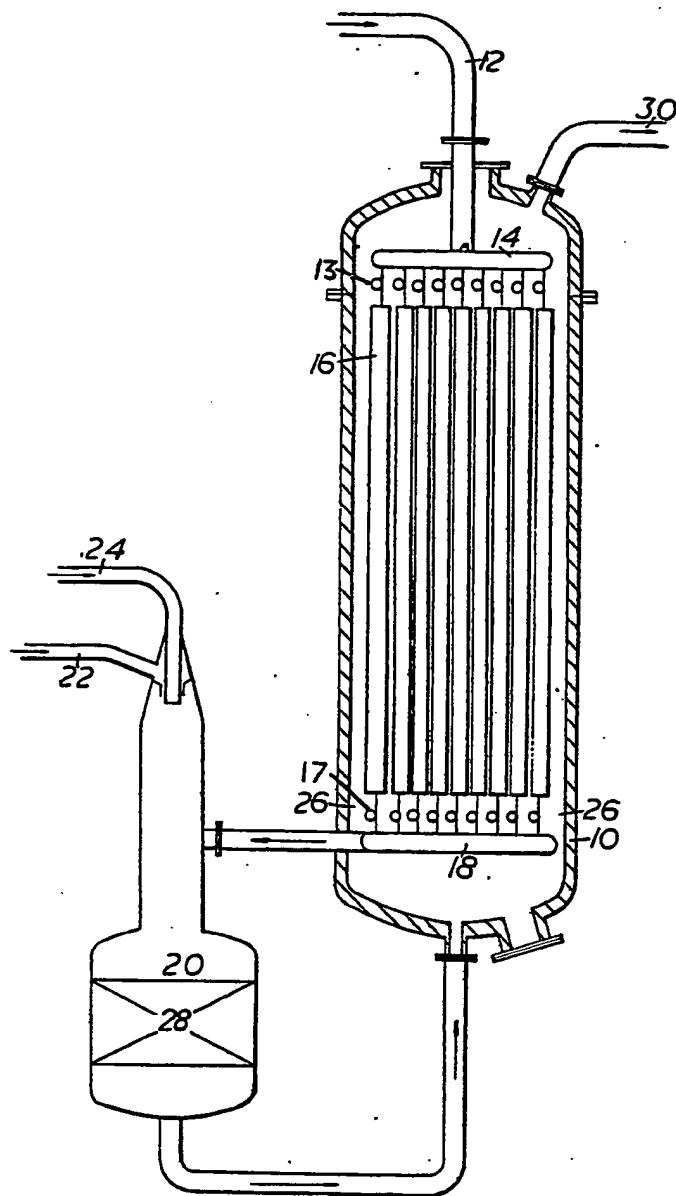
Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.  
—1967. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2,  
from which copies may be obtained.

1093943

COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of  
the Original on a reduced scale*



**THIS PAGE BLANK (USPTO)**